Appln. No.: 10/051,995
Amendment Dated December 21, 2004
Reply to Office Action of September 22, 2004

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Remarks/Arguments:

Applicants affirm the election to prosecute claims 1-29 in the original application which are identified as the claims of Group I.

Applicants withdraw the traverse of the election and reserves the right to file one or more divisional applications covering the subject matter of elected claims 30-37.

The Examiner has rejected claims 1-29 under 35 U.S.C. § 112 first paragraph.

Applicants submit the specification of the present application has fully disclosed the subject matter of claims 1-29 in such a way as to reasonably convey to one skilled in the relevant art that the inventors, at the time the application was filed had possession of the claimed invention.

Specifically, the Examiner has asserted that one aspect of the invention is to permit at least 90% by weight of the alkali metal to react with inorganic acid to produce gaseous chlorine, chlorine dioxide and steam, and the application does not describe in sufficient detail how to:

1) Determine the proper stoichiometric ratio to complete both of the two competing reactions, and

2) Ensure that at least 90 wt % of the alkali metal chlorate is reacted with inorganic acid.

Following is a description of two techniques for determining the proper ratio of alkali metal chlorate to inorganic acid. This description makes the reasonable assumption that the inorganic acid is dilute hydrochloric acid and the alkali metal chlorate is sodium chlorate.

One approach is empirical. After constructing a reactor, begin feeding a known flow of dissolved alkali metal chlorate at a know concentration (e.g. 47% by weight) and at temperature and pressure described in the patent application. While holding the flow of chlorate solution constant, feed increasing amounts of inorganic acid into the reactor, waiting sufficient time for the reaction rates to stabilize at each rate of acid feed, considering the volume of the reactor and the liquid flow rates involved.

Continuously monitor the gaseous output of the reactor and the concentration of chlorate ion and acid in the waste stream from the reactor. The gaseous concentrations of chlorine and chlorine dioxide can be measured using a dual wavelength spectrophotometer such as that marketed by The Optek Corporation. Acid concentration in the waste stream can be measured by titration using caustic solution as is common practice in chemical analysis. Chlorate ion concentration can be measured by amperometric titration as described in The "Standard Methods" Handbook published by the American Waterworks Association, or by ion chromatography. When the acid feed increases to the point where the acid concentration in the waste stream begins to increase rapidly with the addition of more acid feed, the reagents are approximately in stoichiometric proportion. At the same time, the concentration of chlorate ion in the waste stream will approach zero.

When the stoichiometric optimum has been determined as described in the previous paragraph, increase the flow of chlorate solution and repeat the optimization of the acid flow. If the acid concentration in the waste stream increases while there are still significant amounts of

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chlorate ion present, then the reaction is not complete before the waste exits the reactor, and optimal capacity of the reactor has been exceeded.

Figure 3 of the above-identified application shows that for each injection of the inorganic acid into a chlorate solution, the reaction continues for proximately 10 minutes at a temperature of about 180 degrees F, with Sodium chlorate concentration of 600 g/L and hydrochloric acid concentration of 37% by weight. This reaction time is a slight function of the concentration of the reagents, and a strong function of temperature, but does not vary much as a function of the degree of completion of the reaction. Therefore, for operation under these conditions, each reactor segment should be designed to have a liquid retention time of at least 10 minutes. If the reaction is still occurring when the next injection of acid occurs, no substantial harm will be done. The slight reaction from the almost-spent acid will simply be added to the strong reaction from the new acid, with, perhaps a small decrease in efficiency. However, if the final reaction is not complete when the waste exits the reactor, severe problems can occur. For example, chlorine and chlorine dioxide can continue to evolve in the waste lines, causing potential corrosion or explosion. For this reason, it is recommended that ample extra retention time be provided after the last injection of acid. Since a reactor disclosed in the specification of the present invention can be a simple pipe, extra length and retention time are not expensive. Because of the potential risks if the reaction continues in the waste stream, it is recommended that the waste stream be diluted with cool water and the pH be raised with a solution of sodium hydroxide, sodium carbonate, or other alkali solutions. These measures assure that any continuing reaction is quenched.

Another method for determining the stoichiometric optimum is as follows:

A) With the reactor and the feed liquids at the temperature described in the present application, begin flowing chlorate solution into the reactor until solution begins to overflow into the waste stream. Then begin flowing acid into the chlorate solution at a rate of two moles of acid per mole of chlorate. Since this ratio is the stoichiometric ratio for reaction 1, and reaction 2 (specification page 19, lines 15-16) requires a higher acid/chlorate ratio, to the extent that reaction 2 occurs, the combination of the two reactions will have less than the stoichiometric ratio of acid/chlorate.

B) Measure the production rate of chlorine dioxide and chlorine. Since all of the chlorine dioxide is produced in reaction 1, it is easy to calculate how much of the chlorine is produced in reaction 1, and one can assume that the rest is produced in reaction 2. Knowing this, it is possible to calculate how much of the chlorate is unreacted between the two reactions.

C) Assume that all of the unreacted chlorate would react in reaction 1, calculate the amount of additional acid that this will require and increase the acid feed by that amount.

D) Repeat steps B & C until the calculations of step B show that there is a negligible amount of unreacted chlorate.

These techniques are applicable regardless of whether the reactor is a single tube with multiple injection points as shown in Figure 1, or a series of reactors as shown in Figure 2.

The foregoing analyses adequately demonstrate that a worker skilled in the art could take possession of Applicants' invention without undue experimentation.

In view of the foregoing it is respectfully submitted that the rejection of claims 1-29 under 35 U.S.C. § 112 is not well taken and should be withdrawn.

The Examiner has rejected claim 5 under 35 U.S.C. § 112 second paragraph alleging there is no antecedent basis for the phrase "said aqueous solution of alkaline metal chloride". Applicant has amended claim 5 to correct the obvious typographical error where the term chloride was inadvertently substituted for the term chlorate. Therefore, it is respectfully submitted that the rejection of claim 5 under 35 U.S.C. § 112 is not well taken and should be withdrawn.

The Examiner has rejected claims 1, 7 under 35 U.S.C. § 102(b) over Swindells et al. U.S. Patent 4,081,520. The fundamental difference between the cited patent and the present invention is that the cited patent uses a reducing agent methanol. The reducing agent produces a different reaction from the one used in the present application.

The Swindell reaction is:

$$2NaClO_3 + 2H_2SO_4 + CH_3OH => 2ClO_2 + 2NaHSO_4 + HCHO + 2H_2O$$
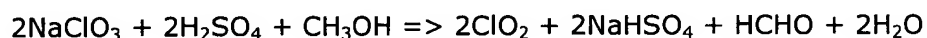
The reducing agent in this reaction is methanol, a toxic product that would be prohibited from use in a drinking water plant where product of the present invention is targeted for use.
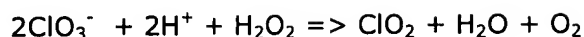
Besides use of a reducing agent used in the '520 Patent the present invention differs in another important aspect. Although the Swindell technology produces small amounts of chlorine, the reactions are intended to (and do) produce essentially no chlorine. In the Swindell patent, for example, the product is 99% chlorine dioxide and <1% chlorine. In the process of the invention, the product contains >33% chlorine, and the process may be adjusted, as described on page 20, line 20 through page 22, line 16 of the present application, to produce much higher ratios of chlorine to chlorine dioxide. This is very important. Since chlorine dioxide is a far more expensive product than chlorine, all previous chlorine dioxide processes have been designed to maximize chlorine dioxide and minimize or eliminate chlorine production. However, chlorine in one form or another is essential for residual disinfection in water distribution systems. There is increasing concern about the safety of transporting and storing large volumes of liquefied chlorine gas, especially in urban areas. The invention allows the production of chlorine as well as chlorine dioxide in proportions that match the disinfection needs of the municipality.

Applicants submit the Examiner has used their teaching to not only select but to interpret the prior art, this being clearly contrary to existing Patent Law.

In view of the foregoing it is respectfully submitted that the rejection of claims 1 and 7 under 35 U.S.C. § 102(b) is not well taken and should be withdrawn.

The Examiner has rejected claims 1-3, 5, and 7 under 35 U.S.C. § 102(e) over Charles et al. Published Application US 2003/0007899. Here again the fundamental difference between the Charles Application and the present invention is that the Charles reference uses a reducing agent, e.g. hydrogen peroxide.

In the Charles application, the reaction is:

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$$2ClO_3^- + 2H^+ + H_2O_2 => ClO_2 + H_2O + O_2$$

This reaction is problematic for several reasons:

A) The production of oxygen leads to foaming in the reactor, which requires rapid removal and dissolution/dilution of the foam. Since the products of the reaction are equal parts of ClO2 and oxygen, the gaseous product is 50% ClO2. It is well known that this mixture can explode spontaneously, if it is not diluted or dissolved in less time than the induction period of ClO2. Since the product is inextricably mixed with the foam, in drinking water applications, the foam must be added to the treated water along with the ClO2. This introduces undesirable contaminants such as acid or chlorate ions into the water. It also wastes reagents that are contained in the foam. In the process of the present invention, no significant foaming has been observed. Only gas phase products exit the reactor.

B) Hydrogen peroxide is unstable and cannot be stored for long periods without degradation of its concentration.

Dr. Gilbert Gordon in his paper "Is All Chlorine Dioxide Created Equal", published in the April 2001 issue of the Journal AWWA has shown that under upset conditions, the Charles reaction can produce large amounts of perchlorate ion. Perchlorate ion is a health risk and is therefore very undesirable in drinking water applications. Dr. Gordon has stated that perchlorate ion will not form in the presence of the significant amounts of chloride ion found in the reactions according to the present invention (e.g. paper pp169, section titled "Summary of Chlorate ion-based systems").

For the reasons set forth above it is respectfully submitted that the rejection of claims 1-3, 5 and 7 under 35 U.S.C. § 102(e) is not well taken and should be withdrawn.

The Examiner has rejected claims 1-29 under 35 U.S.C. § 103(a) over Charles Published Application.

For the reasons set forth above it is respectfully submitted that the teaching of the Charles reference is fatally defective and does not render applicants invention obvious.

Applicant respectfully submits that the Examiner has fallen into the trap of using applicants' own teaching to not only select but to interpret the reference. This is clearly contrary to existing Patent Law.

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In view of the foregoing amendments and arguments it is respectfully submitted that the above-identified application is in condition for allowance and a notice to that effect is earnestly solicited.

Respectfully submitted,

James C. Simmons
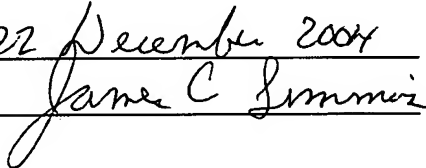
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Dated: December 21, 2004

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22 December 2004
James C Simmons

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Chlorine dioxide (ClO_2) is an alternative oxidant to chlorine for the treatment of drinking water. ClO_2 must be produced on site by the oxidation of chlorite ion or the reduction of chlorate ion. Each generation technology ultimately produces ClO_2; however, the final product (composition and purity) can be very different. Discussions on ClO_2 purity have typically focused on chlorine. Other potential impurities include chlorite ion, chlorate ion, acid, hydrogen peroxide, and in some cases perchlorate ion. Experimental data are presented to show similarities and potential differences in product composition.

IS ALL
chlorine dioxide
CREATED EQUAL?

BY GILBERT GORDON

Chlorine dioxide (ClO_2) is widely used as an alternative to chlorine (Cl_2) for treating drinking water. Numerous ClO_2 generation technologies have recently been developed to improve the conversion efficiency and purity of ClO_2. Researchers continue to investigate the behavior of ClO_2 in these new technologies. The results of this research are not often published; however, a large body of important data is now available to water utility operators who must decide how best to apply high-purity ClO_2 (Gares, 1998; Cramp et al, 1997; Cowley, 1995; Gordon & Rosenblatt, 1995; Burke et al, 1993; Kaczur & Cawlfield, 1993; Miltner, 1976).

Water utilities use ClO_2 for preoxidation (e.g., for iron and manganese), control of taste and odor problems, and inactivation of common pathogens. Because ClO_2 is an oxidizing agent that does not chlorinate, it is often used to lower trihalomethane (THM) concentrations (Gordon et al, 1992) in finished water to meet levels established by the US Environmental Protection Agency (USEPA) (1979).

USEPA encourages the use of chemical oxidants that help to reduce the health risks associated with microbiological sources such as *Giardia* and *Cryptosporidium*. Typically, the benefits of microbiological inactivation far outweigh the chemical risks associated with the use of oxidants such as ClO_2 and ozone (O_3). However, state and federal regulators are still concerned about the health effects of disinfection by-products. This means that the oxidant and any species carried through the treatment train with the oxidant, as well as any by-products formed during disinfection, are important to consider in the context of meeting current and future drinking water regulations.

In contrast to Cl_2, regulations exist that prevent ClO_2 from being shipped (US CFR, 1984) to a utility because of safety reasons. Similar to O_3, this means that ClO_2 must be produced on site. The chemistry of ClO_2 generation can be oversimplified by suggesting that ClO_2 is produced either by reducing chlorate ion (ClO_3^-) or by oxidating chlorite ion (ClO_2^-). In fact, a variety of generation technologies are commercially used to produce ClO_2 (Table 1).

FIGURE 1   Oxidant demand curve—high ClO_2 to ClO_2^- conversion

ClO_2—chlorine dioxide, ClO_2^-—chlorite ion
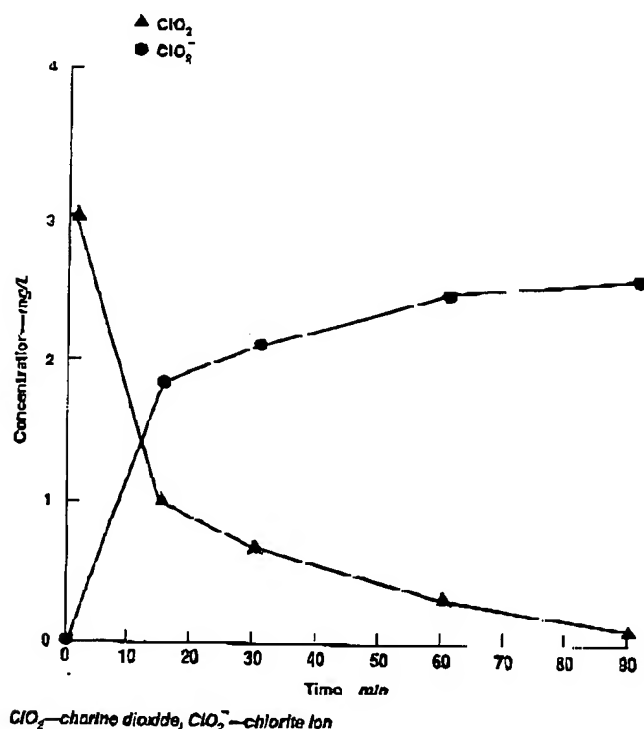
TABLE 1 ClO_2 generation technologies[*]

Chemistry	Comments
ClO_2^-/Cl_2	Aqueous chlorite ion/gaseous Cl_2; aqueous chlorite ion/aqueous Cl_2; solid chlorite ion/gaseous chlorine
ClO_2/H^+	Acid activation
ClO_3/H^+/reducing agent	Large-scale production
$ClO_3/H_2SO_4/H_2O_2$	Small-scale production
Electrochemical (ClO_3^-)	Small-scale production

[*]ClO_2—chlorine dioxide, ClO_2^-—chlorite ion, Cl_2—chlorine, ClO_3^-—chlorate ion, H_2SO_4—sulfuric acid. H_2O_2—hydrogen peroxide

The technologies presented in Table 1 suggest that efficient ClO_2 generation from ClO_2^- (an oxidation process) or ClO_3^- (a reduction process) can be complicated. The chemistry involves generation precursors (e.g., ClO_2^- in liquid or solid form or ClO_3^-), additional oxidizing (or reducing) agents (e.g., Cl_2 or hydrogen peroxide [H_2O_2], acid, electrochemical cells, and various mixing and gas-extraction processes. In each case, the final product contains ClO_2. Typically, generator outputs can be maximized under optimized conditions to produce 95% yields based on the conversion of the starting material. However, this does not mean that the compositions of the generated ClO_2 products are the same. In practice, the composition of the final product can be very different. For example,

• Does the product contain unused excess precursor chemicals (e.g., ClO_2^- or H_2O_2)?

• Are the unused chemicals (ClO_2^-, ClO_3^-, H^+, Cl_2, H_2O_2) continuing to react?

• Is ClO_2 stable in the presence of by-products and/or unused precursor chemicals?

• What by-products are produced and present in the final product mixture?

• Are the available analytical methods capable of distinguishing between oxidant species?

• Are safety and the disposal of waste chemicals important?

ClO_2 is an effective oxidant for treating drinking water. Each technology has a specific chemistry that defines the final ClO_2 product. It is a simplistic overstatement to conclude that each of the generation technologies produces ClO_2 with an identical product composition, purity, and performance capability.

PROPERTIES OF ClO_2

Table 2 lists some of the generally recognized physical properties (Gates, 1998; Kaczur & Cawlfield, 1993; Gordon et al, 1972) of ClO_2. Pure ClO_2 exists almost entirely as the permanent free-radical monomer. The chlorine–oxygen bonds show predominantly double-bond character, forming an angle of about 117.5 degrees with a chlorine-oxygen bond length of 1.47 Å and a dipole moment of 1.69 debye units.

In solution, ClO_2 is a dissolved gas. At 25°C (77°F), ClO_2 is about 23 times as concentrated in the aqueous solution (Tauhe & Dodgen, 1949) than in the gas phase in which it is at equilibrium. Aqueous ClO_2 is light-sensitive (Bowen & Cheung, 1932) and decomposes through free radicals to give ClO_3 and Cl^-.

Reactive species. It is not unusual to simultaneously have multiple chlorine species present in ClO_2 solutions originating from generated by-products or unreacted precursors. Table 3 lists the various chlorine species (Gordon & Bubnis, 1998) that might be present following the generation of ClO_2.
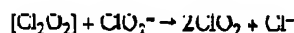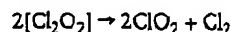
Each chlorine species listed in Table 3 can potentially affect the chemistry of ClO_2, as shown by the examples in Table 4.

Recent advances in ClO_2 generation and purification have helped to increase the purity of ClO_2 used at drinking water utilities. These important developments are the result of a better understanding of how to minimize reactions that lower production efficiency or promote the generation of unwanted (and unintended) by-products.

Important intermediate species. The importance of intermediate species is often neglected (or misunderstood). For example, it is common for field engineers to "tune" liquid/gas generators by simply increasing the feed rate of chlorite ion or Cl_2 (Table 4, Eq 3). The chemistry of this process involves the formation of an intermediate species $[Cl_2O_2]$:

$$ClO_2^- + Cl_2 \rightarrow [Cl_2O_2] + Cl^-$$
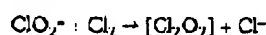
At high concentrations, ClO_2 is primarily formed:

$$2[Cl_2O_2] \rightarrow 2ClO_2 + Cl_2$$

$$[Cl_2O_2] + ClO_2^- \rightarrow 2ClO_2 + Cl^-$$

When the generator has a relatively low initial ClO_2^- concentration, or excess Cl_2, significant amounts of ClO_3^- are formed:

$$[Cl_2O_2] + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+$$

$$[Cl_2O_2] + HOCl \rightarrow ClO_3^- + Cl^- + H^+$$
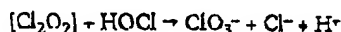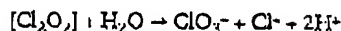
Thus, to efficiently generate and apply ClO_2, the chemistry of the $[Cl_2O_2]$ intermediate must be understood.

Photochemical reactions. The photolysis of ClO_2 is a complex process that results in different products depending on the wavelength of excitation. Wavelengths > 300–436 nm will cause ClO_2 to dissociate (Bowen & Cheung, 1932) and form an intermediate species (H_2ClO_2) that reacts to form ClO_3^-. At wavelengths between 260 and 375 nm, photolysis of ClO_2 forms two energetic species (Taube & Dodgen, 1949)—$ClO(^2\pi)$ and $O(^3P)$. Below 260 nm, ClO_2 photolysis results in a third energetic species, $O(^1D)$. The data suggest the energetic species act as photosensitizers (Gordon & Katakis, 1987). A photosensitizer absorbs photons and transfers the energy to water or intermediates. To accomplish this, the molecule must have a sufficiently long-lived excited state to react bimolecularly and be able to undergo electron-transfer reactions in the excited state.


FIGURE 2   Oxidant demand curve   70% ClO_2 to ClO_2^- conversion

ClO_2—chlorine dioxide, ClO_2^-—chlorite ion, ClO_3^- chlorate ion
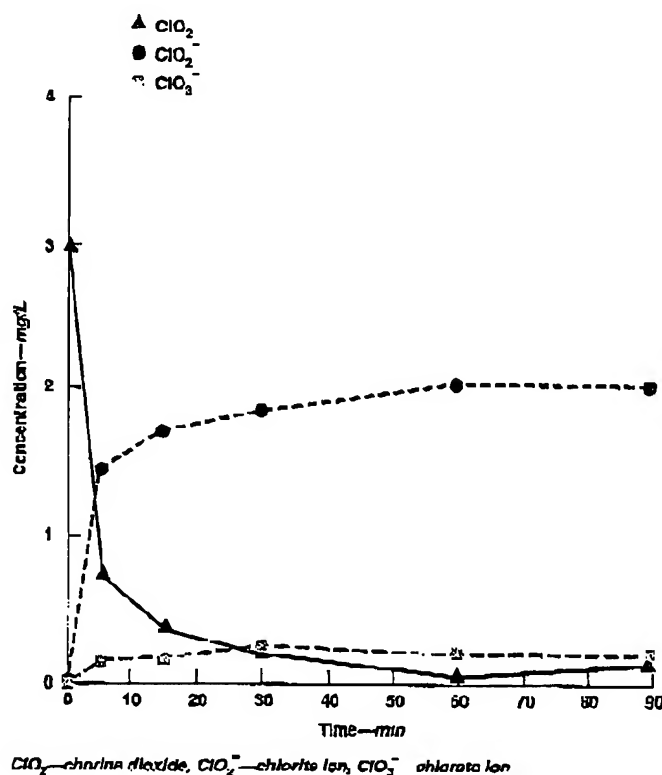
Kinetics versus thermodynamics. Typically, the chemistry that occurs during water treatment does not correspond to simple one-step reactions. The reaction mechanisms can be complex and involve numerous highly reactive intermediate species. On the other hand, thermodynamic predictions can be made on the basis of half-cell data. Consider the following ClO_2 reactions in which the standard potential (Pourbaix, 1966) varies as a function of pH and concentration.

$$ClO_2 + e^- \rightarrow ClO_2^-$$
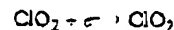
$$E = 1.160 + 0.0591 \log \frac{P_{ClO_2}}{[ClO_2^-]}$$

$$ClO_2 + H^+ + e^- \rightarrow HClO_2$$
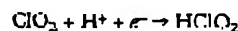
$$E = 1.277 - 0.0591 (pH) + 0.0591 \log \frac{P_{ClO_2}}{[HClO_2]}$$

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$$
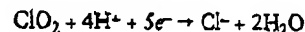
$$E = 1.511 - 0.0473 (pH) + 0.0118 \log \frac{P_{ClO_2}}{[Cl^-]}$$

TABLE 2   Physical properties of chlorine dioxide

Property	
Molecular weight	67.45
Melting point	–59°C (–75°F)
Boiling point	11°C (51°F)
Solubility limit, 25°C, 34.5 mm Hg	~3 g/L
ΔG^0 at 25°C (77°F)	2.95 kcal/mol
ΔH^0 at 25°C (77°F)	25 kcal/mol
ΔS^0 at 25°C (77°F)	43.9 eu (aq)
Partition coefficient, 35°C (95°F)	21.5
Molar absorptivity, 360 nm	1,225–1,250 cm$^{-1}M^{-1}$

TABLE 3   Chlorine oxidation states

Oxidation State	Species	Formula
+7	Perchlorate ion	ClO_4^-
+6		
+5	Chlorate ion	ClO_3^-
+4	Chlorine dioxide	ClO_2
+3	Chlorite ion	ClO_2^-
	Chlorous acid	$HClO_2$
+1	Hypochlorite ion	OCl^-
	Hypochlorous acid	$HOCl$
0	Chlorine	Cl_2
–1	Chloride ion	Cl^-

Because ClO_2 is a very reactive oxidant, a chemical understanding of the thermodynamics and kinetics is needed to maximize generator efficiency and minimize unwanted by-products during generation and storage.

A general discussion of the properties and reactions of ClO_2 is the starting point for maximizing ClO_2 generation and minimizing unwanted by-products. Several generation processes are available, and utilities can choose the best generation process based on their regulatory and disinfection needs. The following discussion presents the results of studies designed to understand the extent of unused precursor chemicals and the formation of by-products relevant to each ClO_2 generation technology.

EXPERIMENTAL PROCEDURES

Ion chromatography (USEPA method 300; Pfaff et al, 1991) was used for all ClO_2^- and ClO_3^- measurements. The samples were purged with nitrogen in order to displace ClO_2 and then were further treated with ethylenediamine. The samples (25–200 μL) were injected into the eluent at 1.0 mL/min. With this method, the samples passed through a metal-free column to remove dissolved metals and a guard column before separation on the analytical column. An anion micromembrane suppressor was

used with a weak sulfuric acid (H_2SO_4) regenerant solution flowing at 10 mL/min.

Perchlorate ion was measured using ion chromatography according to the method that was developed at the California Department of Health (Okamoto et al, 1999). All other oxidant measurements were performed using the methods listed in *Standard Methods* (1998).

The ClO_2 stock solutions for the demand studies were prepared by reacting sodium chlorite ($NaClO_2$) (16% solution, 4 g in 25 mL) with potassium persulfate (4% solution, 2 g in 50 mL) in a gas washing bottle that was continuously purged with nitrogen. The output of the reaction, ClO_2, was collected in chilled water in the dark. The molar absorptivity (Gordon & Rosenblatt, 1995) (ϵ) of ClO_2 is 1,250$M^{-1}cm^{-1}$. However, it is well known that the $^2B_1 - ^2A_2$ electronic transition of ClO_2 appears as a series of absorbance maxima (Vaida & Richard, 1991a; Vaida & Richard, 1991b) over the 320–400-nm region. Thus, the accurate standardization of ClO_2 stock solutions using UV–Vis spectrophotometry depends on the ability of the spectrophotometer to resolve the ClO_2 fingerprint (Gauw et al, 1999). This means that ϵ should be determined specifically for each individual spectrophotometer.

ClO_2 GENERATION TECHNOLOGIES

For water treatment, commercial ClO_2 generators can be broadly classified as ClO_2-based, ClO_3^--based, or electrochemical systems. The differences between each generation method are governed to a large extent by the generation chemistry (kinetics and thermodynamics).

Chlorite ion–based generation. The oxidation of chlorite ion is the most widely used method for preparing ClO_2 in the drinking water industry. One of the first commercially available generators used acid to convert chlorite ion to ClO_2. Some confusion in the literature exists as to whether the chemistry is best described using chlorous acid or chlorite ion. For simplicity, the process can be described by the following equation:
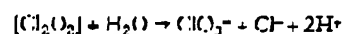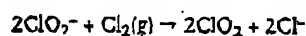
$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O$$
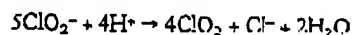
The stoichiometry of this disproportionation reaction ($5ClO_2^- \rightarrow 4ClO_2$) shows that 20% of the original starting material does not produce ClO_2. This means that when all the chlorite ion is consumed, only 80% is converted to ClO_2. In this case, a high conversion efficiency does not result in a high yield. This example also shows why chlorite ion consumption should not be used as the basis for yield calculations.

Typically, ClO_2 is produced by reacting chlorite ion with Cl_2 or $HOCl$.

TABLE 4.   Chlorine species interactions

Chemical Species	Description	Equation Number
Cl⁻	• A reaction product that accompanies ClO_2 formation or decomposition	
	• Can act as a catalyst for certain reactions	
	$HClO_2 + Cl^- \rightarrow [HCl_2O_2^-]$	(1)
	$[HCl_2O_2^-] + Cl^- \rightarrow ClO_2 + \text{other products}$	(2)
Cl_2	• Precursor chemical that reacts with ClO_2^- (or $HClO_2$) to form chlorine dioxide	
	• Excess Cl_2/HOCl slowly reacts with ClO_2	
	$Cl_2 + 2ClO_2^- \rightarrow 2ClO_2 + 2Cl^-$	(3)
	$Cl_2 + ClO_2 + H_2O \rightarrow ClO_3^- + Cl^- + 2H^-$	(4)
HOCl	• Precursor chemical that reacts with ClO_2^- to form chlorine dioxide	
	$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^-$	(5)
OCl⁻	• Reacts with ClO_2^- to form chlorate ion	
	$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$	(6)
ClO_2^-/ClO_2	ClO_2 reaction $ClO_2 + \text{substrate} \rightarrow ClO_2^-$	(7)
	Acid release $5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^- + 2H_2O$	(8)
	Electrolysis $ClO_2^- \rightarrow ClO_2 + e^-$	(9)
	Disproportionation $2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$	(10)
ClO_3^-	• Sometimes a ClO_2 precursor	
	• Sometimes a disinfection by-product	
	$2ClO_3^- + 4H^+ + 2Cl^- \rightarrow 2ClO_2 + Cl_2 + 2H_2O$	(11)
	$2ClO_3^- + H_2SO_4 + H_2O_2 \rightarrow 2ClO_2 + O_2 + SO_4^2 + 2H_2O$	(12)
	$[Cl_2O_2] + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+$	(13)
	$ClO_2^- + HOCl \rightarrow ClO_3^- + Cl^- + H^+$	(14)
ClO_4^-	• Impurity in bulk sodium chlorate	
	• Unwanted by-product	
	Electrolysis $ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$	(15)
	High acidity $8HClO_3 \rightarrow 4HClO_4 + 2H_2O + SO_2 + 2Cl_2$	(16)

$$2ClO_2^- + Cl_2(g) \rightarrow 2ClO_2 + 2Cl^-$$

or $$2ClO_2^- + HOCl \rightarrow 2ClO_2 + Cl^- + OH^-$$

The general stoichiometric equations for the reaction of chlorite ion with Cl_2 do not show the importance of the intermediate species, Cl_2O_2.

$$Cl_2 + ClO_2^- \rightarrow [Cl_2O_2] + Cl^-$$
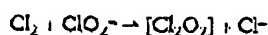
At high reactant concentrations, the intermediate is formed very rapidly.

$$2[Cl_2O_2] \rightarrow 2ClO_2 + Cl_2$$

or $$[Cl_2O_2] + ClO_2^- \rightarrow 2ClO_2 + Cl^-$$
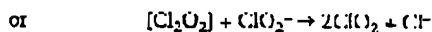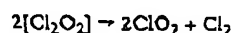
At low initial reactant concentrations, primarily chlorate ion is formed.

$$[Cl_2O_2] + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+$$

The stoichiometry of the undesirable reactions that form chlorate ion is as follows:

$$ClO_2^- + HOCl \rightarrow ClO_3^- + Cl^- + H^+$$

$$ClO_2^- + Cl_2 + H_2O \rightarrow ClO_3^- + 2Cl^- + 2H^+$$
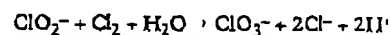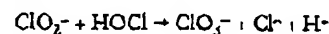
Three-feed system. ClO_2 is readily produced at pH < 3.5. In practice, many utilities use liquid bleach (OCl⁻) as their chlorine source. The pH of liquid bleach is maintained at pH > 11 to prevent decomposition to chlorate ion (Gauw et al, 1999).

$$OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$$

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$$
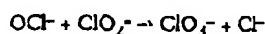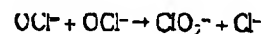
To lower the pH, acid and liquid bleach are combined in a reaction zone to produce a mix of HOCl and Cl_2.

TABLE 5　Typical generator composition during normal operation 1,000 mg/L ClO_2

Species	Formula	ClO_2^- based* mg/L	ClO_3^- based† mg/L	Electrochemical mg/L
Chlorine	HOCl/OCl⁻	~5%‡		
Chlorite ion	ClO_2^-			Variable§
Chlorate ion	ClO_3^-	Chlorine dependent	2.5–8.5, 23	
Sulfuric acid	H_2SO_4		3,500	
Hydrogen peroxide	H_2O_2		120	
Perchlorate ion	ClO_4^-		0.1 µg/L	

*Vacuum eduction system
†Sterling Pulp Chemicals, unpublished data (1999)
‡US Environmental Protection Agency generator performance standard (5%)
§Without gas-stripping, high concentrations are probable.

TABLE 6　Nonoptimized generator effluent composition 1,000 mg/L ClO_2

Species	Formula	ClO_2^- based* mg/L	ClO_3^- based† mg/L	Electrochemical mg/L
Chlorine	HOCl/OCl⁻	~5%‡		
Chlorite ion	ClO_2^-	Variable§		Variable§
Chlorate ion	ClO_3^-	Chlorine dependent	9,590	Variable**
Sulfuric acid	H_2SO_4		8,200	
Hydrogen peroxide	H_2O_2		25	
Perchlorate ion	ClO_4^-		7 µg/L	Variable**

*Vacuum eduction system
†Sterling Pulp Chemicals, unpublished data (1999)
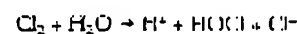‡US Environmental Protection Agency generator performance standard (5%)
§Without gas-stripping, high concentrations can be carried through the system.
** Multiple pass through the electrolysis cell without proper engineering controls and without extraction or penetration can potentially form ClO_3^- and ClO_4^-.

TABLE 7　ClO_2 oxidant demand study—$ClO_2 \rightarrow ClO_2^-$ conversion*

Time min	ClO_2 mg/L consumed	ClO_2^- mg/L measured	Conversion %
0	3.00		
15	2.01	1.84	92
30	2.31	2.12	92
60	2.66	2.51	94
90	2.83	2.63	93

*ClO_2—chlorine dioxide, ClO_2^-—chlorite ion

Chlorite ion is added, and ClO_2 is produced in a second reaction zone. In more recent generator designs, a venturi is positioned after the second reaction zone, and the generated ClO_2 is "extracted" into the water flow.

Two-feed system. Cl_2 gas can be drawn into the water flow through a venturi and combined with chlorite ion metered into a reaction chamber to form ClO_2. In some generators, the hydrolysis of Cl_2 provides acid to neu-

tralize the caustic solution of $NaClO_2$.

$$Cl_2 + H_2O \rightarrow H^+ + HOCl + Cl^-$$

A second method combines gaseous Cl_2 with chlorite ion in a reaction chamber attached to a venturi that "extracts" the ClO_2 into the water flow.

Solid chlorite ion system. In addition to the aqueous chlorite ion feed systems, a solid chlorite ion system has been commercialized. This approach was developed to minimize the presence of Cl_2 in the generated ClO_2. Indications are that optimized systems will generate < 1% Cl_2 in the final product.

This system uses a packed bed of solid $NaClO_2$ imbedded with inert stabilizing components. Dilute, moist Cl_2 is passed through the bed where it reacts with chlorite ion. Because Cl_2 and air are continuously passing over the solid bed, the generated ClO_2 is swept off the bed and carried through to a holding tank. The Cl_2 feed onto the bed can be controlled so that minimal unreacted Cl_2 is able to pass through the bed. This system controls the production of ClO_2 via the delivery of Cl_2.

Summary of chlorite ion-based systems. The primary objective of chlorite ion oxidation processes is to produce ClO_2 at a high conversion efficiency with minimal impurities. The acid activation process is inherently inefficient; however, this does not preclude its use. The simplicity of this process must be balanced against the 20% loss of chlorite ion conversion.

The chemistry of Cl_2 reacting with chlorite ion to form ClO_2 implies that a number of factors must be controlled to achieve a high conversion rate. In systems that do not use gas eduction, it is common to have carry-through of unreacted chemicals in the generator effluent. When conversion efficiencies are low, many operators increase the Cl_2 feed. This makes sense when the Cl_2 flow is below the stoichiometric amount required for 100% conversion. When Cl_2 is in excess, some of it will pass into the water stream through the

venturi. The presence of Cl_2 can also lead to increased chlorate ion levels.

Chlorate ion–based generation. A new low-capacity chlorate ion reduction system (Crump et al, 1997) is now available to drinking water utilities. This system uses excess H_2O_2 and H_2SO_4 to produce ClO_2 with the following reaction stoichiometry:

$$2ClO_3^- + H_2SO_4 + H_2O_2 \rightarrow 2ClO_2 + O_2 + SO_4^{2-} + 2H_2O$$
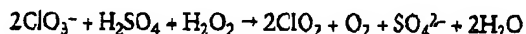
The optimized production of ClO_2 requires excess acid for efficient $ClO_3^- \rightarrow ClO_2$ conversion. The H_2O_2-to-H_2SO_4 ratio is very important. The reported "optimized" ClO_2 production empirical rate law shown here is not stoichiometric, indicating that side reactions are probably occurring. This suggests that the conditions of maximum ClO_2 production are not necessarily the conditions that minimize by-products.

$$R_{ClO_2} = 1.4 \times 10^{17} \exp(-12230/T) \, [H_2SO_4]^{4.4} \, [NaClO_3]^{1.2} \, [H_2O_2]^{0.6}$$

The implication of the optimized model equation (Burke et al, 1993) is that the product stream will likely be acidic; in the case of an upset (low H_2O_2), very acidic. The model also suggests that the "purity" (ClO_2 without the presence of unused reactants) of the ClO_3^--generated ClO_2 could be a problem (e.g., acid and H_2O_2).

Drinking water utilities using chlorate ion reduction methods need to be concerned with perchlorate ion. Sources of perchlorate ion include commercial sodium chlorate ($NaClO_3$) solutions (50–200 mg/L ClO_4^-) used in the reactor. A second source of ClO_4^- occurs when ClO_3^- is present under highly acidic reaction conditions, especially with H_2SO_4:

$$8HClO_3 \rightarrow 4HClO_4 + 2H_2O + 3O_2 + 2Cl_2$$
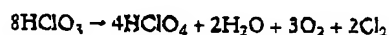
This suggests that the transfer of ClO_2 from the reaction chamber to the holding tank must be controlled. If it is not controlled, ClO_4^- can be "misted" into the generator effluent hold tank. Perchlorate ion concentrations as high as 7–20 µg/L in the generator discharge, which contains 1,000 mg/L ClO_2, have been observed (Sterling Pulp Chemicals, 1999).

Summary of chlorate ion–based systems. The reduction of chlorate ion has long been the method of choice for producing large quantities of ClO_2 for the paper and pulp industries. A small-scale generator suitable for the drinking water industry has the potential for lowering the chemical cost of ClO_2 generation. However, for drinking water purposes, possible regulations relating to H_2O_2 in the generator effluent (not recommended for disinfection), increased acidity (corrosion control), and ClO_4^- formation (potential health risk) may impede its acceptance.

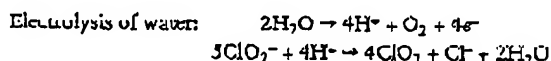**TABLE 8   Sequential oxychlorine speciation**

pH	Chemistry
8	$Cl_2 + 2I^- \rightleftharpoons I_2 + 2Cl^-$ $2ClO_2 + 2I^- \rightarrow I_2 + 2ClO_2^-$
2	$2ClO_2 + 10I^- + 8H^+ \rightleftharpoons 6I_2 + 2Cl^- + 4H_2O$ $ClO_2^- + 4I^- + 4H^+ \rightleftharpoons 2I_2 + Cl^- + 2H_2O$
6M HCl	$ClO_3^- + 6I^- \rightarrow 3I_2 + Cl^- + 3H_2O$

Electrochemical systems. Designs for the electrochemical production of ClO_2 have been commercially available in different forms for many years. Conceptually, electrochemical generators are very simple.
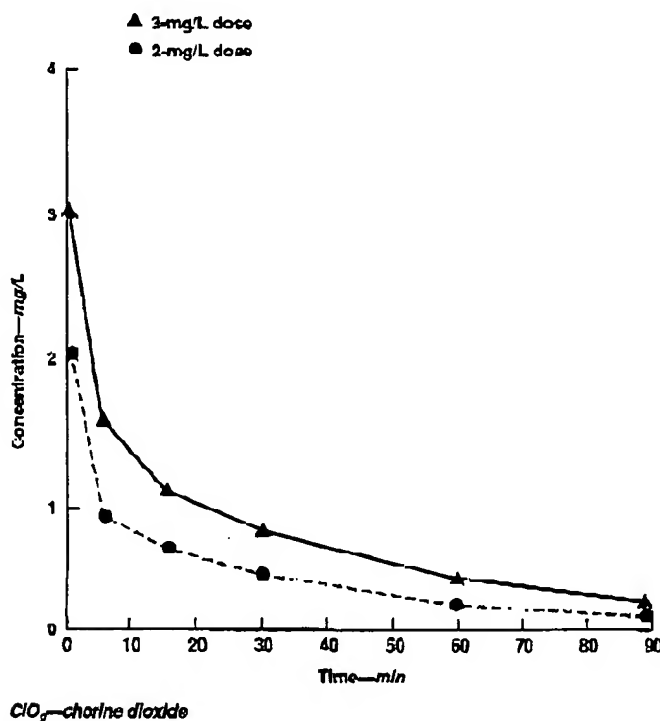
Direct electrolysis: $2ClO_2^- + 2H_2O \rightarrow 2ClO_2 + 2OH^- + H_2$
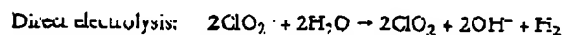
In principle, a single feed solution containing $NaClO_2$ can be metered into the cell. At the anode, the direct electrolysis of ClO_2^- to form ClO_2 takes place. At the cathode, caustic and hydrogen are produced. To prevent further oxidation of ClO_2 to chlorate ion and possibly perchlorate ion as it decomposes in the anolyte, ClO_2 is extracted from the anode (e.g., perextraction or a cascading gas stripper).

Other ways to "electrochemically" produce ClO_2 include the electrochemical production of acid or Cl_2 as a means of supplying precursor chemical to the cell.

Electrolysis of water: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O$

Electrolysis of Cl^-: $2Cl^- + 2e^- \rightarrow Cl_2$
$2ClO_2^- + Cl_2 \rightarrow 2ClO_2 + 2Cl^-$

Electrochemical systems capable of producing 0.5–10 lb/d (0.2–4.5 kg/d) of ClO_2 seem well-suited for small utilities. Efficient ClO_2 transfer from the anode chamber helps to increase the conversion efficiency by enabling unused chlorite ion to be recycled. When a gas-stripping device is used to transfer ClO_2 from the anode to the hold tank, operators need to be aware that acid and possibly Cl_2 can be foamed or "misted" into the hold tank. A second area of concern for operators is the efficiency of the electrochemical cell. In some cases for efficient long-term operation, the cell will require periodic cleaning to remove the buildup of impurities on the electrode surface.

Membrane distillation (perstraction). Because ClO_2 is a dissolved gas in solution, numerous methods for extracting ClO_2 from the reaction chamber have been developed (e.g., gas stripping columns, gas eductors/venturis, low-pressure air flow over a packed bed). Perstraction differs in that a gas-permeable hydrophobic membrane is

FIGURE 3   Oxidant demand curves—two ClO_2 concentrations

▲ 3-mg/L dose
● 2-mg/L dose

ClO_2—chlorine dioxide

This calculation requires the direct measurement of all oxychlorine species. However, this formula ignores the presence of chlorine (free available chlorine = Cl_2, $HOCl$, OCl^-) and perchlorate ion. Conversion efficiency calculated using this formula simply means that unreacted precursor chemicals are minimized in the ClO_2 generator effluent. A high-percent conversion does not mean that a solution has a high purity.

ClO_2 purity. The issue of purity is often confused with conversion. In fact, purity has a very different meaning. Purity refers to the presence of impurities produced or "carried through the system" during generation and the presence of impurities in the ClO_2 product solution. For example, reports that have appeared in the scientific literature suggest that THM formation results from ClO_2 use. Because ClO_2 is an oxidizing agent (a one-electron process, $ClO_2 \rightarrow ClO_2^-$), it does not chlorinate under conditions normally found during drinking water treatment. By comparison, Cl_2 can either be an oxidizing agent or participate in substitution reactions that form THMs. In this case, the reported THMs were probably formed by an impurity in the ClO_2.

Because ClO_2^--based generators are frequently operated below maximum efficiency, a Cl_2 impurity is not unusual. To address this issue, USEPA in April 1999 (USEPA, 1999) suggested a maximum 5% Cl_2 excess for ClO_2 generator effluents.

% excess Cl_2 =

$$\frac{[Cl_2]}{\dfrac{70.91}{2 \times 67.45}[ClO_2 + ClO_2^- + \dfrac{67.45}{83.45}ClO_3^-]} \times 100$$

The weakness of the chlorine purity standard is that it is limited to ClO_2^- and ClO_3^- and does not take into account other oxychlorine species (Table 3).

By-products. The presence of ClO_2^-, ClO_3^-, ClO_4^-, free available chlorine, and acid in generated ClO_2 has a potential cost impact for utilities. If high levels of any of these common by-products are observed, additional treatment may be required to reduce or minimize regulated by-products that would enter the distribution system (e.g., reduced iron for lowering ClO_2^- residuals).

The generation chemistry largely determines which species will be present in the final ClO_2 product stream. For example, Tables 5 and 6 show some of the differ-

used to separate a donor solution (reaction chamber) from an acceptor solution (water flow). By controlling the pressure gradient across the membrane, ClO_2 can be extracted from a chemically complicated reaction mix into the water flow at a purity level that is not achievable with conventional stripping devices.

Perstraction is particularly well-suited for electro chemical generation processes (Cowley et al, 1996). It improves safety by eliminating the need for a vapor phase or carrier gas, and there is no need for vacuum operation. High-purity ClO_2 can be produced economically from processes based on chlorite ion oxidation, chlorate reduction, or the chloric acid–based autocatalytic process.

Conversion efficiency. Conversion efficiency is an important cost consideration. The proposed Disinfectants/Disinfection By-Products Rule (*Fed. Reg.*, 1994) addresses this issue for utilities planning to use ClO_2 for preoxidation. However, the final rule (*Fed. Reg.*, 1998) does not contain language requiring a specific conversion efficiency. This situation has caused great confusion in the water industry. The current guideline, as defined by the USEPA in April 1999 (USEPA, 1999), is 95% conversion of ClO_2^- to ClO_2 using the following formula:

$$\% \text{ conversion} = \frac{[ClO_2]}{[ClO_2] + [ClO_2^-] + \dfrac{67.45}{83.45}[ClO_3^-]} \times 100$$

ences in product composition between ClO_2^- based, ClO_3^--based, and electrochemical ClO_2 generators.

A properly tuned generator will have minimal unwanted components in the generator effluent—in other words, high purity. In a simple ClO_2^--based generator not equipped with a gas transfer/delivery apparatus, elevated concentrations of ClO_2^- might be present because of generator inefficiency. The presence of this unreacted precursor can affect the distribution system in a positive or negative way. For example, McGuire and coworkers (1999) reported that ClO_2^- appears to inactivate ammonia oxidizing bacteria and helps control nitrification in

ClO_2^- (Table 7). Oxidant demand results are often reported showing ClO_2 to ClO_2^- conversion ratios in the 70–80% range. This type of data indicates that ClO_2^- continues to react with intermediate species such as $HOCl$, which reform ClO_2 along with ClO_3^-. During this process, some ClO_2^- is also totally reduced to Cl^-. Figures 1–3 show demand profiles often observed in treated water.

The profile provided in Figure 1 (and Table 7) shows a high conversion of ClO_2 to ClO_2^-. The small ClO_3^- residual in high-quality raw water is often (Griese et al, 1992) the result of a photochemical reaction in chlorine-free ClO_2 stock solution, or in some cases, the result of a

The oxidant and any species carried through the treatment train with the oxidant, as well as any by-products formed during disinfection, are important to consider in the context of meeting current and future drinking water regulations.

chloraminated drinking water systems. In contrast, the presence of ClO_2^- in the distribution system is reported (Hoehn et al, 1990) to be responsible for odors in household water supplies caused by ClO_2 "regeneration" at the tap.

Systems equipped with gas transfer/delivery apparatus (vacuum eduction, cascade stripping, or perstraction) can also have impurities such as Cl_2, acid, or H_2O_2 that might continue to react.

Perchlorate ion. The presence of ClO_4^- in drinking water is an important issue. The California Department of Health has established a health advisory for when ClO_4^- concentrations exceed 18 µg/L. Until more health effects data are available, source water wells that show any trace of ClO_4^- are taken out of service.

Because the perchlorate ion issue is relatively new, guidelines have not yet been established by USEPA to advise utilities. USEPA, the US Air Force, and the AWWA Research Foundation are developing strategies (Perchlorate Research Issue Group, 1997) to minimize the effect of ClO_4^- in drinking water. At a minimum, treatment processes that can potentially introduce ClO_4^- into the distribution system should require additional monitoring and the implementation of some type of ClO_4^- removal strategy.

Oxidant demand. The proper way to determine a ClO_2 treatment dose is to perform an oxidant-demand study. For preoxidation applications, ClO_2 is added to the raw water and allowed to react for a prescribed time. Measurements using verified methods (lissamine green B [LGB], amaranth) are then made to determine the difference between the added oxidant dose and the residual oxidant concentration. A more complete study using ion chromatography will also quantitate ClO_2^- and ClO_3^-.

Because ClO_2 oxidation is a one-electron process (the conversion of $ClO_2 \rightarrow ClO_2^-$), a demand study using relatively pure water will show a high conversion ratio to

small amount of chlorine in the ClO_2 stock solution. Figure 2 shows an oxidant-demand profile that might be observed in waters with high concentrations of organic matter. The apparent ClO_2-to-ClO_2^- conversion is lower, demonstrating that ClO_2^- continues to react. The oxidant demand profile in Figure 3 shows the ClO_2 residual for two dose concentrations. The oxidant demand typically increases with time and must be defined for a given dose concentration, contact time, temperature, and pH. These factors make it difficult to extrapolate oxidant demand data from one set of concentrations to another.

The information from a demand study is helpful for calculating $C \times T$ credits for compliance purposes. It also helps in understanding the residual ClO_2^- concentration that can be expected in the treated water.

ANALYTICAL METHODS

Numerous analytical methods for measuring the oxyhalogen species that accompany ClO_2 production appear in *Standard Methods* (1998). There is a great deal of confusion about these methods and the corresponding, readily available simple test-kit procedures. Because of their nonspecific nature, the methods (e.g., iodometry, DPD) are general oxidation methods and are subject to varying levels of interference (Gordon, et al, 1992; Aieta et al, 1984).

It is not uncommon for utility operators to use titration methods (Gordon et al, 1992; Hoehn et al, 1990) to measure oxyhalogen species. Typically, the sample is reacted with iodide ion (I) to form iodine (I_2). Depending on the pH, as shown in Table 8, successive titrations are performed, and individual species concentrations are calculated by difference.

The I_2 titration procedure requires an understanding of chemistry and a higher level of skill to make reliable measurements. This is especially true for ClO_2 concentrations at the milligram-per-litre level. The presence of additional impurities (oxidants such as H_2O_2) can result

in drifting titration endpoints and large analysis errors because of iodide ion oxidation and iodate ion (IO_3^-) formation. If IO_3^- is formed, the titration stoichiometry changes, and measurement errors can be expected. In addition, there is no accounting for the excess I_2 liberated by H_2O_2.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$
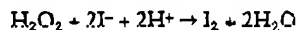
The accurate measurement of ClO_2 and ClO_2 by-products in multicomponent oxidant media requires more advanced instrumentation and a relatively high degree of skill. Three colorimetric methods are widely used for measuring ClO_2 residual concentrations: LGB (Chiswell & O'Halloran, 1991), amaranth (Emmert et al, 2000), and chlorophenol red (CPR) (Sweetin et al, 1996). Each method is capable of measuring ClO_2 at the 0.1-mg/L level. DPD is not recommended for ClO_2 measurement (Gordon et al, 2000) because the DPD species monitored at 515 nm can continue to react to form a colorless product (i.e., the color fades). ClO_2-treated water samples always contain ClO_2^- and typically free available chlorine as a residual disinfectant in the distribution system. Thus, each sample type (i.e., generator effluent, finished water at the plant and in the distribution system) should be evaluated for chlorite ion and chlorine interference. LGB and amaranth use an ammonia/ammonium chloride buffer system to mask any potential chlorine interference and are the methods of choice. Chlorite ion does not interfere in either of these methods. In contrast, CPR exhibits both a chlorine and ClO_2^- interference. Thus, a masking agent such as oxalic acid must be used to remove chlorine. However, when the ClO_2^- concentration exceeds the ClO_2 concentration, an unacceptable interference can be expected (Sweetin et al, 1996).

Even relatively selective methods can potentially suffer from interferences in multicomponent ClO_2 solutions. Thus, methods that selectively mask a potential interference or kinetically discriminate between ClO_2 and the interference have been developed (Gordon, 1998). In extreme cases, the ClO_2 can be diffused through a membrane (Hollowell et al, 1985) (e.g., gas diffusion flow injection analysis) before analysis.

The accurate measurement of ClO_2 by-products at the 0.1–1-mg/L level is difficult using titration methods and is very operator-dependent. The preferred and strongly recommended methodology for the direct low-level measurement of ClO_2^-, ClO_3^-, and ClO_4^- is ion chromatography (Okamoto et al, 1999; Pfaff et al, 1991).

ClO_2 TRANSFER/DELIVERY ISSUES

Technologies that extract ClO_2 from a complicated reaction mixture can be used to enhance product purity. In systems that do not use some type of gas transfer, unreacted reagents being carried through to the point of application might be observed. Gas transfer also helps to prevent ClO_2 from reacting before application. For example, small utilities that are changing to ClO_2 for disinfection might consider using a small electrochemical system to generate ClO_2. In electrochemical systems, ClO_2^- is oxidized to ClO_2 as the reagent flows through the anode. By removing ClO_2 with a gas transfer device, any unreacted ClO_2^- can be recirculated back through the anode, thereby increasing the cell conversion efficiency. Without gas transfer, recirculation of the anolyte will result in chlorate ion formation. Continued recirculation of the "unstripped" feed solution without the proper engineering controls can potentially lead to perchlorate ion formation at high cell current. Because the way in which chlorite ion feed is consumed is an important cost consideration, operators should be aware of the chemistry taking place in the anode: chlorite ion to ClO_2 conversion, chlorate ion formation, possible perchlorate ion formation, acid generation, and chlorine generation.

When gas-transfer devices are used, it is important to determine the effect of other components that might also be stripped over into the product stream. In some ClO_3^--based generators, H_2O_2 and/or acid can be stripped out of the reaction mix (Tables 5 and 6). If H_2O_2 and ClO_2 are present in solution, they readily react in neutral or even slightly acidic solutions (pH > 4):

$$2ClO_2 + H_2O_2 + 2OH^- \rightarrow 2ClO_2^- + O_2 + 2H_2O$$
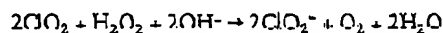
The data (Ni & Wang, 1996) in Table 9 show short-term conversion of $ClO_2 \rightarrow ClO_2^-$ in the presence of H_2O_2. The data (Sterling Pulp Chemicals, 1999) in Table 10 show that when ClO_2 and H_2O_2 are present in solution in equal concentrations at drinking water pH, the ClO_2 conversion to ClO_2^- can be as high as 50% of the starting concentration after 2 h. These data confirm that ClO_2 and H_2O_2 are not compatible oxidants because they react. By comparison, ClO_2 and Cl_2 or HOCl are more compatible species because they react much more slowly. If H_2O_2 is carried over during gas stripping and enters the finished water, compliance could be an issue because H_2O_2 is not a recognized residual disinfectant. In addition, most utilities would have difficulty determining the presence of H_2O_2 in the finished water because of the absence of appropriate analytical methods.

A second important issue is to determine to what extent does the "stripped" H_2O_2 in the generator effluent react with ClO_2. If the amount of H_2O_2 present in the generator effluent is 10% of the ClO_2 concentration (Tables 5 and 6), a substantial amount of ClO_2 is reduced and unavailable for application.

The presence of acid can also affect the quality of the finished water. It is not unusual for a gas stripper to "mist" acid over into the hold tank. If the generation

product is a foam, very high concentrations of acid can be expected. The effect of increased acid is twofold. In recent years, a number of new regulations have been promulgated by USEPA to control corrosion. High acidity added during treatment can make it necessary for a utility to implement treatment steps to maintain pH and control corrosion in the distribution system. A second area of concern is the potential for acid to promote perchlorate ion formation. Chlorate ion under highly acidic conditions can react (possibly via disproportionation) to form perchlorate ion. The current California (and potentially USEPA) view is to shut down water supplies that introduce ClO_4^- into the finished water.

SAFETY

A drinking water utility must consider many safety issues when it decides to use ClO_2. Clearly, the generator must be properly designed to prevent runaway reactions, have adequate safety venting, and have a high tolerance for overpressure and temperature.

Utilities must also be concerned about worker safety when storing and handling ClO_2. Processes that are operated at high temperatures and pressure should be carefully monitored. If the generator effluent is acidic, appropriate guidelines for handling the product need to be established and regularly reviewed.

The training of utility personnel on the proper handling (including the cleanup of spills) and storage of bulk precursor chemicals ($NaClO_2$, $NaClO_3$, Cl_2, H_2SO_4, or H_2O_2) should be in place before the start of on-site ClO_2 generation.

CONCLUSIONS

The experimental data show that the generation technology used to produce ClO_2 largely determines the composition and purity of the generator effluent. On the basis of these findings, the following conclusions can be drawn:

• Impurities in the generator effluent can react with ClO_2 (e.g., H_2O_2 to form ClO_2^-) and substantially lower the concentration of stored ClO_2 or potentially form unwanted by-products (e.g., acid–perchlorate ion; chlorine–chlorate ion).

• ClO_2 transfer technologies that do not use membrane separation may not eliminate the transfer of impurities in some cases.

TABLE 9 Effect of H_2O_2* on ClO_2 concentrations in distilled, deionized water—1 mg/L ClO_2, 0.24 mg/L H_2O_2, 15°C (59°F)

Reaction Time s	pH 5.5 % loss	pH 6 % loss	pH 6.5 % loss	pH 7 % loss	pH 7.5 % loss
1	0.1	0.3	1.0	3.1	8.9
2	0.2	0.6	2.0	0.1	17.9
3	0.3	0.9	3.8	8.7	23.5
4	0.4	1.2	4.7	11.7	27.6
6	0.6	1.8	6.4	15.3	32.9
8	0.8	2.4	8.0	18.7	35.9
10	1.0	3		21.6	37.7
5 min	20	34	38.7	38.7	40.8

*H_2O_2—hydrogen peroxide, ClO_2—chlorine dioxide

TABLE 10 Longer-term effect of H_2O_2 on ClO_2 concentrations in distilled water at drinking water pH

Reaction Time min	pH	Initial ClO_2* mg/L	H_2O_2 mg/L	Final ClO_2 mg/L	Final ClO_2^- mg/L
120	8.2	1.0	0	0.9	0
121	8.2	1.0	0.1	0.3	0.5
188	7.0	1.0	0.1	0.4	0.6

*ClO_2—chlorine dioxide, H_2O_2—hydrogen peroxide, ClO_2^-—chlorite ion

• Perchlorate ion is a potential by-product in ClO_3^--based generators.

• The current USEPA percent conversion calculation should be adjusted to include additional impurities that can be found in generator effluent (e.g., chlorine, H_2O_2, acid, and perchlorate ion).

• Appropriate analytical methods need to be used to accurately assess ClO_2 purity.

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